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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a lithium rechargeable battery, and relates to the lithium rechargeable battery which adopted as the detail more the organic electrolytic solution and this which cell capacity, cold storage nature, and a charge-and-discharge cycle property are not only improvable, but can improve an elevated-temperature property and a self-discharge property.

[0002]

[Description of the Prior Art] Recently, the miniaturization of electronic equipment, thin-shape-izing, and lightweight-ization are made quickly, and portable electronic devices, such as a laptop type, a computer, a camcorder, and a cellular phone, have also spread quickly.

[0003] High performance-ization is demanded also from the rechargeable battery which supplies power for taking to a miniaturization [of such electronic equipment], lightweight-izing, and thin shape-ized inclination. That is, it replaces with an existing lead accumulator or an existing nickel-cadmium battery, while small lightweight is formed, an energy density is high, and development of the lithium rechargeable battery in which charge and discharge are possible is advancing quickly repeatedly.

[0004] A charge mold lithium cell is a cell which was made filled up with the organic electrolytic solution or the polymer electrolyte with which a lithium ion can move the matter in which the intercalation of a lithium ion and gene TAKARESHON are possible between the anode plate, the cathode and the anode plate which are used as an active material, and cathode, and was manufactured, and a lithium ion generates electrical energy in said anode plate and cathode by the oxidation at the time of an intercalation / gene TAKARESHON, and the reduction reaction.

[0005] as the anode plate of a charge mold lithium cell -- Li/Li⁺ electrode potential -- about 3 - 4.5V -- although high potential is shown and the multiple oxide of the transition metals and the lithium in which the intercalation / gene TAKARESHON of a lithium ion are possible is mainly used, lithium cobalt oxide, lithium nickel oxide, and lithium manganese oxide are mentioned as the example.

[0006] Moreover, structural as cathode, and the lithium metal which can accept a lithium ion reversibly, maintaining an electrical property, or can be supplied, a lithium alloy or the carbon system matter with which the chemical potential at the time of the intercalation / gene TAKARESHON of a lithium ion was almost similar with the metal lithium is mainly used.

[0007] It is called lithium metal cell to use a lithium metal and its alloy as a cathode active material, and it is called lithium ion battery to use a carbon material. The lithium ion battery with which a carbon material is used for it as a cathode active material in order to solve this since the lithium metal cell which uses a lithium metal and an alloy as cathode has a short battery life -- the volume change of a lithium metal occurs when charge and discharge advance, a lithium deposits locally from a lithium surface of metal, and cell short ** occurs -- its stability is low and it is hard to commercialize it was developed. a lithium ion battery only has migration of a lithium ion at the time of charge and discharge -- it is -- an electrode active material -- the original form -- it remains as it is -- since it is maintained, a battery life and stability improve compared with a lithium metal cell.

[0008] Moreover, although a lithium rechargeable battery is carried out having been enough distinguished according to the electrolytic class, the lithium rechargeable battery which uses a solid-state polymer electrolyte especially is called lithium-polymer battery, and a lithium-polymer battery can be classified into the perfect solid-state mold lithium-polymer battery which uses the perfect solid electrolyte with which the organic electrolytic solution is not contained at all by the class of polymer electrolyte, and the gel mold lithium-polymer battery which uses the gel mold polymer electrolyte which infiltrated the organic electrolytic solution into the polymer. Moreover, a lithium-polymer battery is

also classifiable into a lithium ion polymer battery and a lithium metal polymer battery with the ingredient used as a cathode active material as mentioned above.

[0009] Said organic electrolytic solution is an important element which opts for the engine performance of not only a lithium ion battery but a lithium-polymer battery. the organic electrolytic solution is the ion conductor made to dissolve lithium salt in an organic solvent, and receives the conductivity of a lithium ion, and an electrode -- it should excel in chemical and electrochemical stability. And it should become low cost at that an usable temperature requirement should spread and coincidence. Therefore, though ionic conductivity and a dielectric constant are high, it is desirable to use an organic solvent with low viscosity.

[0010] However, although the mixed organic solvent system which mixed the organic solvent of hypoviscosity is used for the organic solvent of a high dielectric constant since the single organic solvent in which is made to satisfy the above conditions and it deals does not exist, as the example, the mixed solvent of the carbonate system mixed solvent; ethylene carbonate of propylene carbonate and diethyl carbonate, dimethyl carbonate, and diethyl carbonate is mentioned.

[0011] When such a mixed organic solvent is used, there is the advantage to which ionic conductivity is greatly improved and the initial capacity of a cell becomes large when the mobility of a lithium ion increases, but since the electrolytic solution is oxidized with a cathode active material as a cycle advances, there is a trouble that the capacity of a cell decreases, and when the mobility of a lithium ion falls by frazil of an organic solvent, there is a possibility that ionic conductivity may fall rapidly, at low temperature.

[0012] By JP,7-169504,A, in order to raise the ionic conductivity in low temperature, the organic electrolytic solution with which the freezing point added the 3rd component solvent like very low methyl propionate and ethyl propionate to the two-component system organic solvent which consists of a conventional high dielectric constant solvent and a conventional hypoviscosity solvent is indicated. However, in this case, although it improves, the life property in ordinary temperature falls, and a low-temperature discharge property has the trouble which the electrolytic solution is polluted by the product by the spontaneous reaction with a charge collector, and has bad effect on a cell property by it.

[0013] Moreover, as lithium salt used for the organic electrolytic solution of a current lithium rechargeable battery, they are LiClO₄, LiBF₄, LiPF₆, and LiCF₃SO₃. Or LiN₂(CF₃SO₂) Although it is, this has poor thermal stability and ionic conductivity has a low trouble. On the other hand, it is LiPF₆. Although ionic conductivity is excellent, since it is very sensitive to moisture, it has the trouble that the electrolytic solution itself is easy to disassemble.

[0014]

[Problem(s) to be Solved by the Invention] The technical technical problem which this invention tends to attain does not react easily with a cathode active material, is excellent in the charge-and-discharge cycle property of a cell, and is offering the organic electrolytic solution with which the low-temperature property's has been improved.

[0015] Other technical technical problems which this invention tends to attain are offering the organic electrolytic solution in which is made to improve the elevated-temperature property and self-discharge property of a lithium rechargeable battery, and it deals.

[0016] When other technical technical problems adopt said organic electrolytic solution as the pan which this invention tends to attain, it is offering the lithium rechargeable battery by which the charge-and-discharge cycle property, the low-temperature property, the elevated-temperature property, and the self-discharge property have been improved.

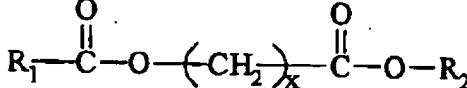
[0017]

[Means for Solving the Problem] The technical technical problem of this invention is attained by following the (1) - (14) by The means for solving a technical problem (invention) of a publication.

[0018] (1) The organic electrolytic solution characterized by said mixed organic solvent containing the compound shown with a high dielectric constant solvent, a hypoviscosity solvent, and the following chemical formula 1 in the organic electrolytic solution containing a mixed organic solvent and lithium salt.

[0019]

[Formula 2]



[0020] The inside of said formula, and R1 And R2 It is independent-like mutually, and is the alkyl group of a carbon number 1 thru/or the linearity of 3, or an annulus, and x is the integer of 1 thru/or 4.

[0021] (2) The organic electrolytic solution given in the above (1) whose mixed volume ratio of said high dielectric constant solvent, a hypoviscosity solvent, and the compound of said chemical formula 1 is characterized by being 30-

50:30-40:20-30.

[0022] (3) The organic electrolytic solution given in the above (1) characterized by being one or more compounds chosen from the group which said high dielectric constant solvent becomes from ethylene carbonate, propylene carbonate, and a gamma butyrolactone.

[0023] (4) The organic electrolytic solution given in the above (1) characterized by being one or more compounds chosen from the group which said hypoviscosity solvent becomes from dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, dimethoxyethane, and a tetrahydrofuran.

[0024] (5) The organic electrolytic solution given in the above (1) characterized by being one or more compounds chosen from the group which the compound of said chemical formula 1 becomes from dimethyl malonate, diethyl malonate, dimethyl succinate, a dimethyl GURUTA rate, and dimethyl horse mackerel **-TO.

[0025] (6) The organic electrolytic solution given in the above (1) whose content of said lithium salt is characterized by being one mol per 1l. of organic electrolytic solutions thru/or 1.5 mols.

[0026] (7) The organic electrolytic solution given in the above (6) characterized by being one or more compounds chosen from the group which said lithium salt becomes from inorganic substance system lithium salt and organic substance system lithium salt.

[0027] (8) The organic electrolytic solution given in the above (7) said whose lithium salt is characterized by being the mixture of inorganic substance system lithium salt and organic substance system lithium salt.

[0028] (9) The organic electrolytic solution given in the above (8) said whose inorganic substance system lithium salt is characterized by being fluorine system lithium salt.

[0029] (10) Said organic substance system lithium salt is LiC(CF₃ SO₂)₃ and LiN (C₂ F₅ SO₂)₂. And LiN₂ (CF₃ SO₂) The organic electrolytic solution given in the above (8) characterized by being one or more compounds chosen from the becoming group.

[0030] (11) The organic electrolytic solution given in the above (8) whose mole ratio of said inorganic substance system lithium salt and said organic substance system lithium salt is characterized by being 0.7-0.9:0.3-0.1.

[0031] (12) The organic electrolytic solution given in the above (1) characterized by including further the inorganic substance additive of 1x10⁻⁴ - 5x10⁻² mol concentration.

[0032] (13) Said inorganic substance additive is LiBO₂, Li₂ CO₃, Li₃ PO₄, Li₃ N, and SnO₂. The organic electrolytic solution given in the above (12) characterized by being one or more compounds chosen from the becoming group.

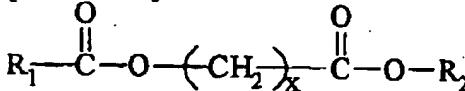
[0033] (14) The lithium rechargeable battery characterized by including the anode plate containing the oxide or the sulfide of a lithium content metal, the cathode containing a lithium metal, a lithium alloy, or carbon material, and the organic electrolytic solution of any one publication of above-mentioned (1) - (13).

[0034]

[Embodiment of the Invention] In the electrolytic solution for lithium rechargeable batteries containing a mixed organic solvent and lithium salt, the technical technical problem of this invention is accomplished with the organic electrolytic solution characterized by including the compound in which said mixed organic solvent is shown with a high dielectric constant solvent, a hypoviscosity solvent, and the following chemical formula 1, and it deals in it.

[0035]

[Formula 3]



[0036] The inside of said formula, and R₁ And R₂ It is independent-like mutually, and is the alkyl group of a carbon number 1 thru/or the linearity of 3, or an annulus, and x is the integer of 1 thru/or 4.

[0037] In the electrolytic solution for lithium rechargeable batteries containing a mixed organic solvent and lithium salt, other technical technical problems of this invention are made including the compound in which said mixed organic solvent is shown with a high dielectric constant solvent, a hypoviscosity solvent, and the following chemical formula 1 with the electrolytic solution for lithium rechargeable batteries characterized by said lithium salt being the mixture of inorganic substance system lithium salt and organic substance system lithium salt, and it deals in them.

[0038] Moreover, further, other technical technical problems of this invention are made by the lithium rechargeable battery containing the anode plate containing the oxide or the sulfide of a lithium content metal, the cathode containing a lithium metal, a lithium alloy, or carbon material, and the organic electrolytic solution of above this inventions, and it deals in them.

[0039] Although characterized by the organic electrolytic solution for attaining the technical problem of the beginning

of this invention containing the compound displayed on said chemical formula 1, since oxidation reaction with an electrolyte and a cathode active material is controlled and it is not easily decomposed under the high voltage, said compound can be contributed to improving the charge-and-discharge cycle property of a cell. Moreover, since the melting point is very low, it can contribute also to an improvement of the low-temperature property pointed out as a serious fault of a lithium cell.

[0040] When the compound displayed on said chemical formula 1 is illustrated concretely, there are dimethyl malonate, diethyl malonate, dimethyl succinate, a dimethyl GURUTA rate, and dimethyl horse mackerel **-TO.

[0041] Moreover, the dielectric constant of the high dielectric constant solvent used for the organic electrolytic solution of this invention is 30 or more, and, as for a hypoviscosity solvent, it is desirable for viscosity to be 1.5 or less cPs.

[0042] One or more compounds chosen in ethylene carbonate, propylene carbonate, or a gamma butyrolactone as a high dielectric constant solvent used for the organic electrolytic solution of this invention are desirable, and it is desirable that they are one or more compounds chosen from the group which consists of dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, dimethoxyethane, and a tetrahydrofuran as a hypoviscosity solvent.

[0043] As for the mixed organic solvent used for the organic electrolytic solution of this invention, it is desirable for the mixed volume ratio of the compound displayed on said high dielectric constant solvent, a hypoviscosity solvent, and a chemical formula 1 to be 30-50:30-40:20-30.

[0044] The lithium salt used for the organic electrolytic solution for attaining the technical technical problem of the beginning of this invention is lithium salt by which well-known was carried out to this industry, and may contain one or more chosen from the group which consists of an inorganic substance system and organic substance system lithium salt.

[0045] Inorganic substance system lithium salt is lithium salt which does not contain carbon at a chemical structure ceremony, for example, is LiClO₄, LiBF₄, and LiPF₆. It is.

[0046] Organic substance system lithium salt is lithium salt which contains carbon in a chemical structure type, for example, is LiCF₃ SO₃, LiN(CF₃ SO₂)₂, LiC(CF₃ SO₂)₃, and LiN(C₂ F₅ SO₂)₂. It is.

[0047] As for the total content of the lithium salt contained in the organic electrolytic solution, it is desirable that they are one mol per 1l. of organic electrolytic solutions thru/or 1.5 mols. It is because the ionic conductivity of lithium salt appears most highly in said range within the organic electrolytic solution.

[0048] On the other hand, the organic electrolytic solution for attaining the second technical technical problem of this invention is excellent in inorganic substance system lithium salt and thermal stability, and is characterized by raising a low-temperature discharge property and a self-discharge property by mixing the organic substance system lithium salt seldom influenced of moisture at a fixed rate.

[0049] Although the inorganic substance system lithium salt in which is used for the mixture of said inorganic substance system lithium salt and organic substance system lithium salt, and it deals will not be specially restricted if it is a lithium compound which is dissociated in an organic solvent and takes out a lithium ion, its fluorine system lithium salt which was excellent in electrical characteristics also in it is desirable.

[0050] The organic substance system lithium salt in which is used for the mixture of said inorganic substance system lithium salt and organic substance system lithium salt, and it deals is LiN(CF₃ SO₂)₂ and LiC(CF₃ SO₂)₃. And LiN₂(C₂ F₅ SO₂) One or more compounds chosen from the becoming group are desirable. Since said compound has high pyrolysis temperature and is seldom influenced of moisture, it carries out the role which raises the elevated-temperature property and self-discharge property of the organic electrolytic solution.

[0051] It is desirable that it is 0.7-0.9:0.3-0.1 in a mole ratio, when the mole ratio of organic substance system lithium salt is 0.3 or more, the ionic conductivity of the electrolytic solution falls rapidly, the capacitance characteristics of a cell become a defect, and to the case of 0.1 or less, the self-discharge property of the ratio of said inorganic substance system lithium salt and organic substance system lithium salt does not improve.

[0052] Moreover, the organic electrolytic solution of this invention may contain an inorganic additive further in order to raise a self-discharge property further. As said inorganic additive, it is LiBO₂, Li₂ CO₃, Li₃ PO₄, Li₃ N, and SnO₂. Although it can be used, a lithium way acid compound (LiBO₂) is the most desirable also in it. For example, the valence has non-bonding electron by 3, and a boron atom carries out the role of the electron acceptor which is going to take an electron from the carbon of a cathode active material. Therefore, the bonding strength of carbon and boron becomes considerably large, and the inclination for the chemical potential of cathode to increase and to accept a lithium ion further arises, so that this bonding strength increases. It is that the concentration of the lithium ion in cathode increases and the capacity of a cell increases after all. The addition of the inorganic additive for demonstrating such effectiveness has per [1x10⁻⁴] 1l. of organic electrolytic solutions thru/or desirable 5xten - two mols.

[0053] The organic electrolytic solution of this invention is applicable also to the lithium ion polymer battery

possessing a gel mold giant-molecule solid electrolyte. That is, it is applicable to all the lithium rechargeable batteries except a perfect solid-state mold lithium-polymer battery.

[0054]

[Example] Hereafter, an example and the example of a comparison are given and this invention is explained more to a detail. However, it is not that this invention is restricted only to the following example.

[0055] LiPF₆ used in the following example and the example of a comparison Do not refine the cell reagent class product of Nihonbashi book incorporated company, it is used, and they are LiC (CF₃ SO₂)₃ and LiN (C₂ F₅ SO₂)₂. And LiN₂ (CF₃ SO₂) Did not refine the 3M company cell reagent class product, and it was used. The solvent used at the time of organic electrolytic-solution manufacture is the cell reagent class product of Merck Co. (Merck), and all experiments were conducted under the argon gas (99.9999% or more) ambient atmosphere.

After putting in the reagent bucket with which the ethylene carbonate of a solid state entered into the example 1 electric-type mantle, it heated at 70-80 degrees C gradually, and they was made to liquefy. Subsequently, it is 1M LiPF₆ to the plastics bucket which keeps the electrolytic solution. LiPF₆ of the content which can make a solution After putting in, dimethyl carbonate was put in and the shake dissolved said lithium metal salt violently. The shake mixed equally the ethylene carbonate solution liquefied here, adding using a pipet, dimethyl malonate was added as a compound of a chemical formula 1 here, and the shake mixed the solution equally strongly. Under the present circumstances, the volume ratio of ethylene carbonate, dimethyl carbonate, and dimethyl malonate was set to 40:40:30.

[0056] After keeping the organic electrolytic solution manufactured as mentioned above for 20 days in a dry box, the moisture content in said organic electrolytic solution was measured using the Karl Fischer titration method (use device: Switzerland metronome company 737KF KURO meter). The moisture content in a water measurement result and the organic electrolytic solution was 20 ppm of outlines.

[0057] If it removed having used diethyl malonate instead of dimethyl malonate as a compound of the example two-generations study type 1, it manufactured by the same approach as an example 1.

[0058] If it removed having used dimethyl succinate instead of dimethyl malonate as a compound of example 3 chemical formula 1, it manufactured by the same approach as an example 1.

[0059] If it removed having used the dimethyl GURUTA rate instead of dimethyl malonate as a compound of example 4 chemical formula 1, it manufactured by the same approach as an example 1.

[0060] If it removed having used dimethyl horse mackerel **-TO instead of dimethyl malonate as a compound of example 5 chemical formula 1, it manufactured by the same approach as an example 1.

[0061] If it removed having set the mixed volume ratio of example 6 ethylene carbonate, dimethyl carbonate, and dimethyl malonate to 40:40:20, it manufactured by the same approach as an example 1.

[0062] If it removed having set the mixed volume ratio of example 7 ethylene carbonate, dimethyl carbonate, and dimethyl malonate to 50:30:20, it manufactured by the same approach as an example 1.

[0063] If it removed having not added dimethyl malonate to an example of comparison 1 mixing organic solvent, the electrolytic solution was manufactured by the same approach as an example 1. Under the present circumstances, the volume ratio of ethylene carbonate and dimethyl carbonate was set to 1:1.

[0064] If it removed having set the mixed volume ratio of example of comparison 2 ethylene carbonate, dimethyl carbonate, and dimethyl malonate to 60:20:20, the electrolytic solution was manufactured by the same approach as an example 1.

[0065] If it removed having set the mixed volume ratio of example of comparison 3 ethylene carbonate, dimethyl carbonate, and dimethyl malonate to 30:30:40, it manufactured by the same approach as an example 1.

[0066] The ionic conductivity, cold storage property, and potential window property of the organic electrolytic solution manufactured by said examples 1-7 and the examples 1-3 of a comparison were evaluated. Under the present circumstances, said characterization was carried out by the following approaches.

[0067] 1) The non-blocking (non-blocking) measurement cel was assembled in the ionic conductivity dry box of the electrolytic solution. in order to intercept that use about 15ml of electrolytic solutions and the platinum electrode which it is going to measure, and a cel contacts air -- reagent storage -- public funds -- it was kept in the group thin film case. the cel kept by said metal thin film case -- the exterior -- taking out -- constant temperature -- after keeping it with a constant humidity chamber for 1 hour, conductivity was evaluated by measuring an impedance with an impedance measurement machine.

[0068] 2) After having put this container into the TABAI thermo hygrometer after having closed the cover, having rolled the perimeter of a cover with the paraffin film, after preparing two plastic envelopes for the cold storage properties of 30ml and putting the 15ml electrolytic solution into each container, and making contact of air intercept completely, and leaving it respectively for 24 hours at the temperature of -30 degrees C and -40 degrees C, the freezing propriety of the

electrolytic solution was observed with the naked eye.

[0069] 3) The potential window range was measured using the potential scan measuring method (cyclicvoltammetry) to the organic electrolytic solution of the potential window examples 1-7 and the examples 1-3 of a comparison. 3 pole measurement cel was used and the carbon electrode and the lithium metal electrode were used respectively. The scan speed was made into 1 mV/sec on the frequency of 1MHz. The measurement result was shown in drawing 1.

[0070] 4) In order to evaluate the charge-and-discharge life property of the cell which used the organic electrolytic solution manufactured by the charge-and-discharge life property examples 1-7 and the examples 1-3 of a comparison, the 2016 type coin mold cell (refer to drawing 3) was manufactured as follows.

[0071] After mixing the polytetrafluoroethylene dissolved in LiCoO₂, Super-P carbon (M. M.M.Carbon Co. product), and N-methyl pyrrolidone, manufacturing a paste type anode plate active material and casting this for aluminium foil with a thickness of 200 micrometers, it was dried and stuck by pressure, and it cut and the anode plate 34 for coin mold cells was manufactured.

[0072] Moreover, after casting for aluminium foil with a thickness of 200 micrometers this after mixing the polytetrafluoroethylene dissolved in graphite powder (MCMB 2528 and Osaka Gas Co. product), Super-P carbon (M. M.M.Carbon Co. product), and N-methyl pyrrolidone and manufacturing a paste type cathode active material and drying and sticking it by pressure, it cut and the cathode 33 for coin mold cells was manufactured.

[0073] As a separator 35, Celgard 2400 (Cellgard 2400) of a hex TOSERA needs company (Hoechst Cellanese Co.) was used, the separator was placed between cathode and an anode plate, and it dipped in the organic electrolytic solution of examples 1-7 and the examples 1-3 of a comparison for 10 minutes. The 2016 type coin mold cell (drawing 3) which took this out after 10 minutes and was completely sealed using the clamp machine by the case 31 made from stainless steel, the cover 32 made from stainless steel, and the insulating gasket 36 was manufactured. At this time, the capacity of a cell was 3.15mAh(s).

[0074] The capacity after initial capacity, 100, and a 200 cycle charge-and-discharge experiment was measured to the coin mold cell manufactured as mentioned above, and it was shown as contrasted with initial capacity. The charge-and-discharge machine (Maccor product) of 1A capacity was used, charge and discharge were respectively carried out by 0.2C at 25 degrees C, and charge electrical potential differences were 3.0-4.2V.

[0075] The ionic conductivity, cold storage property, and charge-and-discharge life property of the organic electrolytic solution manufactured by examples 1-7 and the examples 1-3 of a comparison were shown in Table 1 by the approach mentioned above.

[0076]

[Table 1]

区分	イオン伝導度 (25°C、S/cm)	低温貯蔵特性		充放電寿命特性		
		-30°C	-40°C	初期容量 (mAh)	100 サイク ル後初期容 量対比	200 サイク ル後初期 容量対比
実施例 1	1.124×10^{-2}	非凍結	非凍結	2.89	92%	87%
実施例 2	1.226×10^{-2}	//	//	2.91	90%	85%
実施例 3	1.137×10^{-2}	//	//	2.88	90%	86%
実施例 4	1.123×10^{-2}	//	//	2.86	91%	87%
実施例 5	1.118×10^{-2}	//	//	2.84	90%	85%
実施例 6	1.116×10^{-2}	//	//	2.85	90%	86%
実施例 7	1.133×10^{-2}	//	//	2.87	91%	85%
比較例 1	1.420×10^{-2}	凍結	凍結	2.88	93%	87%
比較例 2	1.475×10^{-2}	//	//	2.91	85%	79%
比較例 3	1.112×10^{-2}	非凍結	非凍結	2.77	82%	75%

[0077] The lithium ion battery which adopted the organic electrolytic solution and this by this invention has a high ionic conductivity value more than at 1×10 to 2 S/cm, and the result of said table 1 and drawing 1 shows excelling in a cold storage property altogether. Moreover, it turns out that the capacity of a cell can maintain the cell property by

which the potential window field was stabilized also in the large and wide range electrical-potential-difference range when there was little capacity rate of change according to cycle advance at 85% or more 100 cycles after in 90% or more of initial capacity contrast and 200 cycles after, it turned out that it excels in a life property very much and drawing 1 was referred to.

[0078] They are 0.9M LiPF6 as example 8 lithium salt. And 0.1M LiC3 (CF3 SO2) LiPF6 of the content which can make a solution LiC3 (CF3 SO2) If it removed having used it, having used ethyl methyl carbonate as ethylene carbonate and a solvent for hypoviscosity, and having used dimethyl succinate as the 3rd solvent as a high dielectric constant solvent, the organic electrolytic solution was manufactured by the same approach as an example 1.

[0079] If it removed having used the dimethyl GURUTA rate as the example 9 3rd solvent, the organic electrolytic solution was manufactured by the same approach as an example 8.

[0080] If it removed having used dimethyl horse mackerel **-TO as the example 10 3rd solvent, the organic electrolytic solution was manufactured by the same approach as an example 8.

[0081] Example 11LiPF6 LiC3 (CF3 SO2) If it removed having set the content to 0.8M and 0.2M respectively, the organic electrolytic solution was manufactured by the same approach as an example 8.

[0082] Example 12LiPF6 LiC3 (CF3 SO2) If it removed having set the content to 0.7M and 0.3M respectively, the organic electrolytic solution was manufactured by the same approach as an example 8.

[0083] LiBO2 of example 132x10-2M If it removed having added further, the organic electrolytic solution was manufactured by the same approach as an example 8.

[0084] The volume ratio of ethylene carbonate and dimethyl carbonate is set to 2:1, without adding example of comparison 4 ethyl methyl carbonate, and it is LiC (CF3 SO2)3. It is 1M LiPF6, without adding. If it removed having used it, the organic electrolytic solution was manufactured by the same approach as an example 8.

[0085] Ethyl methyl carbonate was used instead of example of comparison 5 dimethyl carbonate, and if it removed having set the volume ratio of ethylene carbonate and ethyl methyl carbonate to 1:1, the organic electrolytic solution was manufactured by the same approach as the example 4 of a comparison.

[0086] Example of comparison 6LiPF6 LiC3 (CF3 SO2) If it removed having set the content to 0.6M and 0.4M respectively, the organic electrolytic solution was manufactured by the same approach as an example 8.

[0087] It measured by the same approach as the approach which mentioned above the ionic conductivity and the potential window property of the organic electrolytic solution which were manufactured by said examples 8-13 and the examples 4-6 of a comparison, and was shown in Table 2 and drawing 2.

[0088]

[Table 2]

区分	イオン伝導度 20°C、S/cm	電位窓領域、V
実施例 8	1.124×10^{-2}	5.12
実施例 9	1.126×10^{-2}	5.04
実施例 10	1.137×10^{-2}	4.98
実施例 11	1.223×10^{-2}	5.19
実施例 12	1.118×10^{-2}	5.02
実施例 13	1.216×10^{-2}	5.06
比較例 4	1.133×10^{-2}	4.89
比較例 5	1.220×10^{-2}	4.85
比較例 6	1.112×10^{-2}	4.87

[0089] The organic electrolytic solution (examples 8-13 and examples 4-6 of a comparison) of this invention was applied to the lithium-polymer battery (refer to drawing 4). As a giant-molecule matrix, KINA 2801 (trade name; Kynar [2801], Altochem Co. product) of the copolymer (PVdF-HFP) of poly vinylidene fluoride and hexafluoropropylene was used.

[0090] An anode plate 46 is LiCoO2 of an anode plate active material to acetone 450ml. 65 weight sections, the phthalate dibutyl 20 weight section of a plasticizer, and the KINA 2801 15 weight section were put in, and KINA 2801 was fully dissolved in 50 thru/or 60-degree C oven after *****. After casting so that it may become 120 micrometers in thickness using a doctor blade, after making it mix by the ball mill device for 48 hours, it was made to dry in

atmospheric air and manufactured.

[0091] In the case of cathode 42, it manufactured by the same approach as the time of anode plate manufacture instead of the anode plate active material using the graphite system carbon active material 65 weight section of a cathode active material.

[0092] The separator 43 was manufactured by making it dry in air and volatilizing an acetone, after mixing KINA 2801 30g, dibutyl phthalate 40g, and 30g of silicon oxide to acetone 250ml, and the giant molecule enabled it to fully dissolve in 50 thru/or 60-degree C oven and casting for thickness 50 thru/or 55 micrometers using a doctor blade.

[0093] The lithium ion polymer battery (drawing 4) was manufactured using the anode plate 46 which manufactured as mentioned above, cathode 42, the separator 43, the copper charge collector 41, the aluminum charge collector 45, and the insulating packing material 44.

[0094] 1) a charge-and-discharge life property anode plate active material -- LiCoO₂ it is -- a case -- criteria [mAh/g / 130] -- carrying out -- a cell -- after calculating geometric capacity, it constituted so that the rate of a capacity factor of an anode plate and cathode might be set to 1:2.1 thru/or 2.2. At this time, the capacity of a cell was 170mAh(s) and initial capacity was 177mAh(s). In 2.8 thru/or 4.2V, at the rate of 10 time amount, charge and discharge were carried out twice and degassed.

[0095] The charge-and-discharge cycle of a cell was carried out at the rate of 2 time amount by constant current / constant-voltage conditions 2.8 thru/or 4.2V, and the constant-voltage section was made into 1/10 of the constant current sections. The capacity and the charge-and-discharge cycle-life property of a cell are shown in Table 3.

[0096] 2) The cell manufactured using the organic electrolytic solution of the low-temperature discharge property examples 8-13 and the examples 4-6 of a comparison was charged on constant current / constant-voltage conditions to 4.2V with the rate of 2 time amount. After leaving the charged cell at -20 degrees C for 17 hours, it discharged to 2.75V at the rate of 0.5 time amount. The result was shown in Table 3.

[0097] 3) in order to evaluate the capacity percentage reduction by the self-discharge of the cell which used the organic electrolytic solution of the self-discharge property examples 8-13 and the examples 4-6 of a comparison -- formation -- after charging the cell which the phase completed on constant current / constant-voltage conditions to 4.2V with the rate of 5 time amount, it was made to discharge at the rate of 5 time amount Moreover, after leaving it for 30 days at 20 degrees C, it was made to discharge at the rate of 2 time amount to 2.75V, after charging on constant current / constant-voltage conditions to 4.2V with the rate of 2 time amount. The experimental result was shown in Table 3.

[0098]

[Table 3]

区分	低温放電特性(-20°C)		充放電寿命特性(20°C)		自己放電率 (20°C, %)
	放電容量 (mAh)	放電率 (%)	100サイクル 後電池容量 (mAh)	100サイクル 後初期容量 対比(%)	
実施例 8	149.39	84.4	166.03	93.8	10.7
実施例 9	145.86	82.4	161.96	91.5	11.5
実施例 10	139.21	78.6	158.59	89.6	12.6
実施例 11	147.65	83.4	167.62	94.7	9.1
実施例 12	145.45	82.18	166.38	94.0	11.98
実施例 13	151.69	85.7	168.46	95.14	10.87
比較例 4	25.134	14.2	164.08	92.7	14.1
比較例 5	115.23	65.1	154.34	87.2	13.8
比較例 6	97.03	54.8	145.67	82.3	12.9

[0099] From said table 3, when a life property used only inorganic substance system lithium salt as compared with the case where the organic electrolytic solution of the examples 4-6 of a comparison is used for the case where the organic electrolytic solution of examples 8-13 is used, it was alike, and the low-temperature discharge property and the self-discharge property improved, having been improved more, and the elevated-temperature self-discharge property of 60 degrees C also improved by using both organic substance system lithium salt and inorganic substance system lithium salt.

[0100]

[Effect of the Invention] Not only a potential window field is large, but the organic electrolytic solution for lithium rechargeable batteries by this invention is excellent in ionic conductivity and cold storage nature by including the compound displayed with a chemical formula 1, and a charge-and-discharge life property has the advantage of being excellent. Moreover, by reduction of the rate of self-discharge, capacitance characteristics of the organic electrolytic solution of this invention which contains inorganic substance system lithium salt and organic substance system lithium salt at a fixed rate for lithium rechargeable batteries improve, and its discharge property in that thermal stability is excellent and an elevated temperature improves. Therefore, the lithium rechargeable battery which adopts the electrolytic solution of this invention has a large capacity of a cell, and the charge-and-discharge property stabilized even if the cycle advanced not only being shown but cold storage nature, an elevated-temperature property, and its life property of a cell are also good.

[Translation done.]

* NOTICES *

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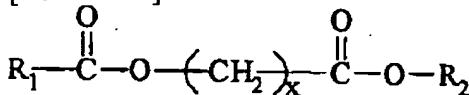
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The organic electrolytic solution characterized by said mixed organic solvent containing the compound shown with a high dielectric constant solvent, a hypoviscosity solvent, and the following chemical formula 1 in the organic electrolytic solution containing a mixed organic solvent and lithium salt.

[Formula 1]



The inside of said formula, and R1 And R2 It is independent-like mutually, and is the alkyl group of a carbon number 1 thru/or the linearity of 3, or an annulus, and x is the integer of 1 thru/or 4.

[Claim 2] The organic electrolytic solution according to claim 1 with which the mixed volume ratio of said high dielectric constant solvent, a hypoviscosity solvent, and the compound of said chemical formula 1 is characterized by being 30-50:30-40:20-30.

[Claim 3] The organic electrolytic solution according to claim 1 characterized by being one or more compounds chosen from the group which said high dielectric constant solvent becomes from ethylene carbonate, propylene carbonate, and a gamma butyrolactone.

[Claim 4] The organic electrolytic solution according to claim 1 characterized by being one or more compounds chosen from the group which said hypoviscosity solvent becomes from dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, dimethoxyethane, and a tetrahydrofuran.

[Claim 5] The organic electrolytic solution according to claim 1 characterized by being one or more compounds chosen from the group which the compound of said chemical formula 1 becomes from dimethyl malonate, diethyl malonate, dimethyl succinate, a dimethyl GURUTA rate, and dimethyl horse mackerel **-TO.

[Claim 6] The organic electrolytic solution according to claim 1 with which the content of said lithium salt is characterized by being one mol per 1l. of organic electrolytic solutions thru/or 1.5 mols.

[Claim 7] The organic electrolytic solution according to claim 6 characterized by being one or more compounds chosen from the group which said lithium salt becomes from inorganic substance system lithium salt and organic substance system lithium salt.

[Claim 8] The organic electrolytic solution according to claim 7 with which said lithium salt is characterized by being the mixture of inorganic substance system lithium salt and organic substance system lithium salt.

[Claim 9] The organic electrolytic solution according to claim 8 with which said inorganic substance system lithium salt is characterized by being fluorine system lithium salt.

[Claim 10] Said organic substance system lithium salt is LiC(CF₃ SO₂)₃ and LiN (C₂ F₅ SO₂)₂. And LiN₂ (CF₃ SO₂)₂ The organic electrolytic solution according to claim 8 characterized by being one or more compounds chosen from the becoming group.

[Claim 11] The organic electrolytic solution according to claim 8 with which the mole ratio of said inorganic substance system lithium salt and said organic substance system lithium salt is characterized by being 0.7-0.9:0.3-0.1.

[Claim 12] The organic electrolytic solution according to claim 1 characterized by including further the inorganic substance additive of 1x10⁻⁴ - 5x10⁻² mol concentration.

[Claim 13] Said inorganic substance additive is LiBO₂, Li₂ CO₃, Li₃PO₄, Li₃ N, and SnO₂. The organic electrolytic solution according to claim 12 characterized by being one or more compounds chosen from the becoming group.

[Claim 14] The lithium rechargeable battery characterized by including the anode plate containing the oxide or the sulfide of a lithium content metal, the cathode containing a lithium metal, a lithium alloy, or carbon material, and the

organic electrolytic solution given in any 1 term of claims 1-13.

[Translation done.]